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in an Fe-Si-Sn-C Alloy

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Introduction

When segregated solute atoms, or atoms chemisorbed from the vapor phase, are found on the surface of a crystal, they are generally found to occupy specific crystallographic sites[1]. Thus it is to be expected that there will be differences in segregation or chemisorption behavior on crystal surfaces of different orientation. Examples of this have been shown by Shelton et al.[2] for the case of C segregation to Ni crystal surfaces and by Johnson et al.[3] for the case of differential segregation of Au to differently oriented surfaces in a poly-crystalline sample of a Ni-Au alloy. We have commenced a study of segregation of the Group IVB elements C, Si, and Sn in Fe, and we report here observations of competitive segregation of these elements to the surfaces of individual grains in a poly-crystalline sample at temperatures up to 700°C.

Experimental Procedure

The vacuum-induction melted alloy was received in the form of a cast ingot of dimensions 2.5x5x1.3 cm (below the hot top), the composition of which is given in Table I. A 3mm slice was cut from the ingot and was hot-rolled at 950°C in 10 passes to 0.6mm. After this 80pct reduction the strip was homogenized at 950°C for 20h. In order to produce a large grain size the strip was given a tensile elongation of 2.5pct (in 10 sec.) and was annealed as indicated in Fig. 1. The sample was then metallographically polished and etched with 3pct Nital. The resulting grain size was in the range .3 to 5mm diam.

The orientations of individual grains were determined by the Laue back-reflection method. The orientations of the grains used for Auger analysis are shown in the standard stereographic triangle in Fig. 2.

The heating method used in the ultra-high vacuum (UHV) system was similar to that employed by Yen et al.[4] The specimen holder is shown in Fig. 3; the specimen was heated by conduction from the resistively heated tungsten ribbons to which it was spot-welded. This configuration gives a reduced electric field in the central portion of the specimen, and it permits Auger analysis at elevated temperatures (with the heating current on). The maximum current used was 20A. A thermocouple spot welded to the back of the specimen was used to control the temperature, which was held constant within $5^{\circ}C$ up to $700^{\circ}C$. The temperature variation over the 10x5mm area of the sample was estimated to be less than $10^{\circ}C$.

The segregation behavior on 9 grains was studied at $50^{\circ}C$ intervals over the temperature range 25 to $700^{\circ}C$. The sample surface was initially sputtered clean with Ar^+ at $25^{\circ}C$; the temperature was then raised to $50^{\circ}C$ and the Auger peak heights were obtained for individual elements using a multi-channel analyser as a function of time until a steady state was reached. Then the temperature was increased by $50^{\circ}C$ and the process was repeated, and up to $700^{\circ}C$; thereupon the process was reversed until the sample returned to $25^{\circ}C$.

The Auger measurements were made with a Physical Electronics scanning Auger Microprobe (SAM) using a primary beam size of 150 μm

at 3keV and 50 μa beam current. The modulation voltage was
6V. The Auger peaks used for analysis were (in eV): Fe 703,
Sn 430, C 270, Si 92, and O 503. It should be noted that the
92eV Si peak contains a contribution of uncertain magnitude
from the 86eV peak of Fe and that the latter decreases
rapidly as the Fe is covered by segregating elements.

Results

Initial Cleaning. The surface composition on grain no. 15
as a function of sputtering time is shown in Fig. 4. This shows
that the surface was initially contaminated with C and O, due to
contact with the air and cleaning in alcohol. It also showed a
small excess of Sn and a corresponding deficiency of Si. How-
ever, the sputtering data for the latter indicates an excess of
Si below the Sn-enriched surface layer. This was our first
direct evidence for a repulsive interaction between Sn and Si
in Fe, which we expected because of the chemical similarity of
these solutes and by analogy with the C-Si repulsion studied
long ago by Darken[5]. The fact that Sn segregated preferentially
with respect to Si, even though the concentration ratio was 1:200
on an atom fraction basis, attests to the greater surface activity
of Sn vs Si. The presence of the Si would be expected to
enhance the surface activity of the Sn because of their mutual
repulsion. This can be rationalized in terms of the Guttmann
regular solution model[6], as shown by McMahon and Marchut[7].

Segregation Behavior

Examples of the apparent steady states reached after prolonged
heating at 450 and 650°C are shown in Fig. 5. At 450°C the
surface coverage by C on grain no. 20 decreased and that of Si

increased. This is in keeping with the anticipated repulsive interaction between these elements in Fe (see above); however, we cannot say anything about the total fractional coverage of the surface or whether the C and Si compete on an individual site basis, as opposed to growth and shrinkage of patches of area containing only C or Si. No Sn segregation was observed at $450^{o}C$ during the time of observation (60 min.); later, this will be shown to be a kinetic limitation.

At $650^{o}C$ (Fig. 5b) Sn segregated strongly on grain no. 15 and reached a steady state within 10h. There was some displacement of Si observed. The amount of Si, if any, remaining after 10h is unknown because of the above-mentioned interference by the Fe 86eV peak.

Large differences were observed in the surface concentration of any element from one grain to another. This can be illustrated by Figs. 6 and 7, each of which shows a different 3-grain junction. Figure 6a is a scanning electron micrograph (SEM) of a junction in the specimen after ageing at $450^{o}C$; the image was formed by detection of absorbed specimen current. Figure 6b is a SAM image formed by monitoring the Si 92eV Auger electrons; it is obvious that grain no. 1 contains much Si, while grains no. 2 and 3 do not. It is interesting that the Si-covered grain appears dark in the SEM; we believe that this is due to a reduction in the work function of the surface due to the Si coverage. This would allow relatively greater emission of secondary electrons from the surface of this grain into the vacuum and would produce a correspondingly smaller specimen current when the electron beam passed over this grain. A similar phenomenon was exhibited when Sn was

allowed to replace the Si by heating at 650°C. Figure 7a is the SEM of a 3-grain junction, and Fig. 7b is the corresponding SAM image; note that the Sn-covered grain is dark in the SEM.

Examples of the segregation behavior of the various elements on different grains over the temperature range studied are shown in Fig. 8. The curves for individual elements on different grains are superimposed in Fig. 9. Certain general similarities are evident: Below 400°C C segregated at the expense of Si; between ~400 and 600°C Si segregated strongly and expelled C from the surface completely; above 600°C Sn segregated strongly and expelled Si from the surface. The Sn concentration decreased when the temperature was raised beyond 650°C; this is consistent with the observation by Lea and Seah[8] that significant evaporation of Sn occurs above that temperature.

When the sample was cooled in 100°C steps, the Sn concentration remained high and Si did not re-appear. Thus, it is concluded that the equilibrium configuration of this alloy involves Sn segregation to the surface; the appearance of Si between 400 and 600°C is presumably the result of its greater diffusivity relative to Sn in that temperature range as shown in Fig. 10. If we consider the peak temperature range for C, Si, and Sn in Fig. 9, we find that these temperatures correspond roughly to a diffusivity of 10^{-13} cm^{-2} sec^{-1}, as indicated by the dashed line in Fig. 10.

As cooling progressed down to 500°C the Sn concentration increased somewhat, implying that surface saturation was being approached as the temperature decreased. Carbon was found to return to the surface below 400°C, but this did not seem to affect the Sn concentration. This implies that interaction between these elements

is not large; presumably the size difference is so large that the similarity of their outer electron configurations is not enough to make them chemically similar.

There were significant differences in the levels of segregation and the temperature positions of the maxima from grain-to-grain, as indicated by Fig. 9. These differences are presumably related to the atomic arrangements on the surfaces of different orientation. The general pattern can be seen if the maximum peak height ratios (PHR), using the Fe 703eV peak as the denominator, are normalized (using the largest value for each element to define 100) and plotted on the standard stereographic triangle. The results, shown in Fig. 11, indicate the presence of a belt in the lower central portion of the triangle in which all three elements reached higher concentrations than in surrounding orientations. However, Si reached its highest concentration on a surface oriented near the (111) corner, whereas the maximum C and Sn concentrations were near their lowest values on this surface.

Discussion

The observations described here were intended to be exploratory and to reveal the areas in which fruitful detailed experiments could be carried out. Primarily, they have raised the question of the basis for the orientation effects portrayed in Fig. 11. The next set of experiments will concentrate on this issue and will employ crystals specially oriented so that their surfaces are well-defined low-index planes, such as (100), (110), and (111). One aspect which deserves particular attention is whether the high index surfaces near the center of the triangle are, in fact, single planes or combinations of steps of lower index planes. If the

latter case prevails, then the total surface coverage
should be understandable in terms of coverages found on the
constituent lower index planes.

Two aspects of the segregation behavior which show up
clearly and which can be understood fairly well even at this
stage of the work are the presence of metastable surface
coverage by faster diffusing elements at lower temperatures and
the presence of strong chemical repulsion between C and Si and
between Si and Sn. The former aspect appears to be the surface
analog of the formation of metastable bulk precipitates during
ageing of a supersaturated solid solution. This kind of phenome-
non has been recognized and studied by physical metallurgists
for many years.

The repulsive chemical interactions are to be expected
between chemically similar elements which do not combine to form
compounds when each is dissolved in a third element. The interesting
feature revealed in the present study is the importance of atomic
s! . differences in determining the degree of chemical repulsion.
The relevant atomic sizes are listed in Table II, in which the
atomic radii are adjusted for a bulk coordination number of 12.
The size differences between C and Si and between Si and Sn
(with respect to Fe) are 32.4pct and 23.7pct, respectively;
whereas it is 56.1pct for the case of C and Sn. Apparently,
the difference in the latter case is so large that these elements
behave somewhat independently as far as surface segregation is
concerned. Presumably, one should not look upon this as only
involving atom size, per se, but also as an effect of size on
the outer electron properties. For example, the outer p electrons

of Sn are certainly bound to the atom less tightly than those of C simply because of their greater distance from the nucleus.

Conclusions

1. In an Fe-based alloy containing 3.1pct Si, 0.06pct Sn, and 0.004pct C each of the solutes was observed to segregate to the surface during heating. As the temperature was raised the dominant element was C, then Si, then Sn, each replacing the previous element. This is presumably a kinetic effect, reflecting the relative diffusivities of these elements in Fe.

2. There are repulsive interactions between C and Si and between Si and Sn in that the presence of one tends to expel or exclude the other from the surface. However, C and Sn seem to behave relatively independently of each other. This is rationalized in terms of the atomic size differences with respect to Fe.

3. The maximum level, and even the temperature range of segregation, of these solutes depend on the crystallographic orientation of the surface. C and Sn appear to follow similar crystallographic preferences, but Si behaves somewhat differently.

Acknowledgements

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TABLE I. Composition of the Sample

Elements	Si	C	S	Sn	Fe
Wt %	3.1	0.004	0.004	0.06	Balance

TABLE II. Atom Size Data Adjusted For Coordination Number 12

	C	Si	Sn	Fe
$r(10^{-8}$ cm)	0.914	1.32	1.62	1.26
Δr	-0.35	+0.06	0.36	0
$\Delta r/r_{Fe}$	-27.6%	+4.8%	+28.5%	0

FIGURE CAPTIONS

1. Annealing schedule for producing coarse-grained specimens.

2. Orientations of surface normals of the grains studied.

3. Details of specimen holder.

4. Variation of surface composition during initial sputtering of one grain showing initial contamination by C and O, small segregation of Sn, and depletion of Si.

5. Examples of variation of surface composition of two grains as a function of time at 450 and 650°C.

6. (a) Scanning electron image (using absorbed specimen current) of a three-grain junction at 450°C. (b) Scanning Auger electron image (using the Si 92eV electrons) showing that the grain with high Si coverage corresponds to the dark grain in (a).

7. (a) Scanning electron image of another three-grain junction at 650°C. (b) Scanning Auger electron image (using the Sn 430eV electrons) showing an effect similar to that in Fig. 6.

8. Examples of variation of steady state surface composition of four grains with equilibration temperature during both heating and cooling.

9. Superposition of curves from Fig. 8 for (a) C, (b) Si, and (c) Sn.

10. Diffusivities of C, Si, and Sn in Fe, extrapolated from data compiled in Ref. 9.

11. Dependence of maximum Auger peak height ratios (normalized to 100) on surface crystallographic orientation for (a) C, (b) Sn, and (c) Si.

Fig 1.

Fig 2

CERAMIC

0.003" x 0.04" TUNGSTEN RIBBON

SAMPLE

STAINLESS STEEL

Cr – Al THERMOCOUPLE

TO DC POWER SUPPLY

Fig. 3

Fig 4.

GRAIN No. 15
650°C

Sn

Fe

Si *

PEAK HEIGHT (arb. units)

7.0

2.0

1.0

0   200   400   600

TIME (min.)

(b)

GRAIN No. 20
450°C

Fe

C

Si

Sn

PEAK HEIGHT (arb. units)

3.0

2.0

1.0

10   20   30   40

TIME (min.)

(a)

Fig 5

2

3

40μ

(a)

Fig. 6.

1

(b)

40μ

(a)

Fig. 7.

(b)

Fig 3

SILICON

CARBON

Tin

Fig. 9.

(b)

(a)

(c)

Fig 10

(a) C

(b) Sn

(c) Si
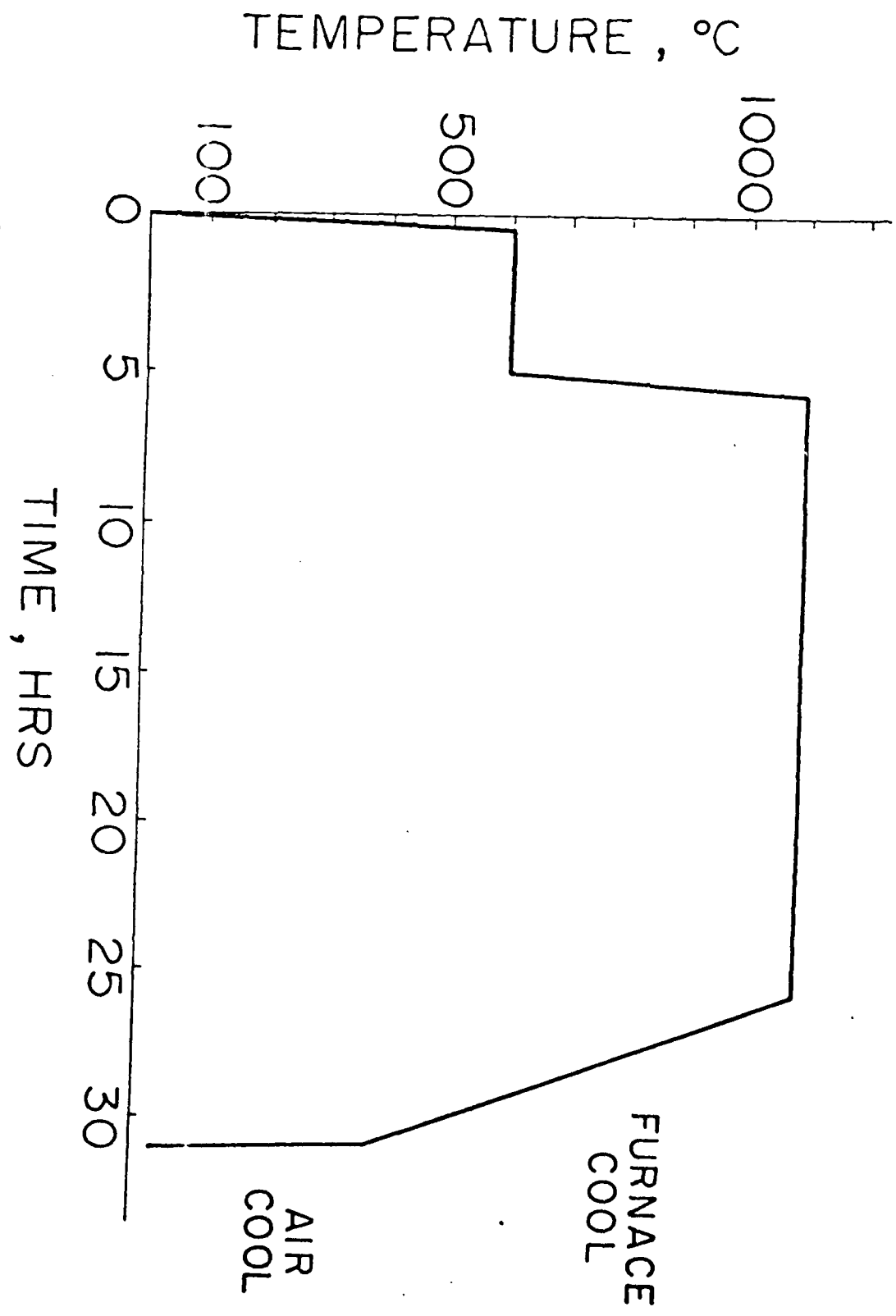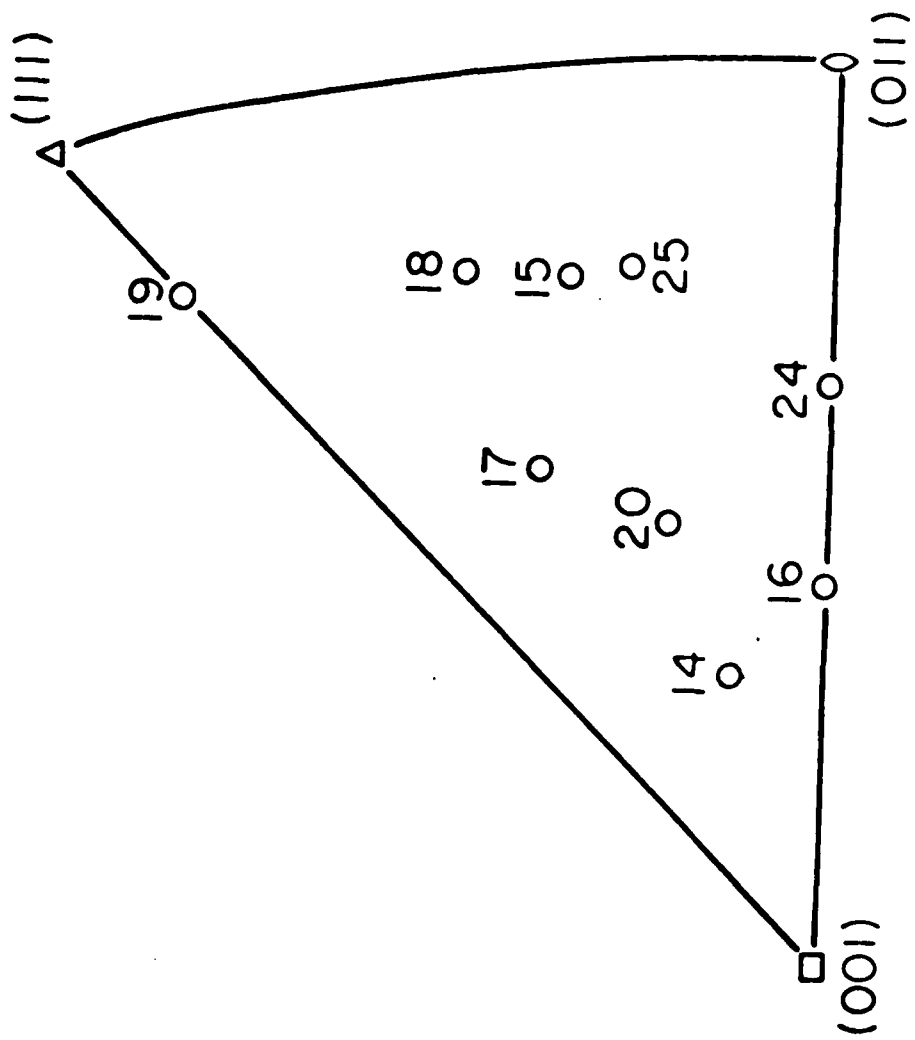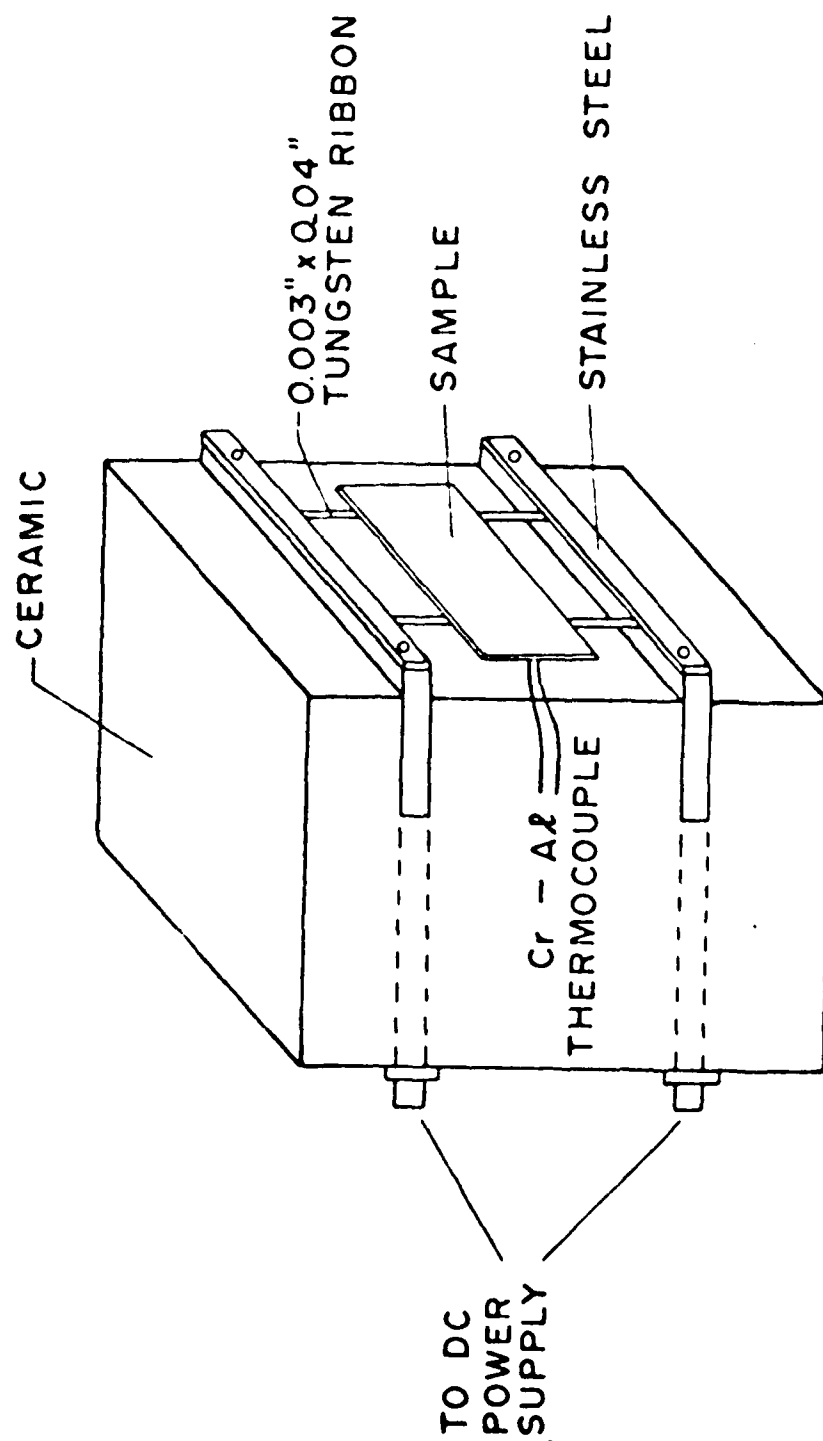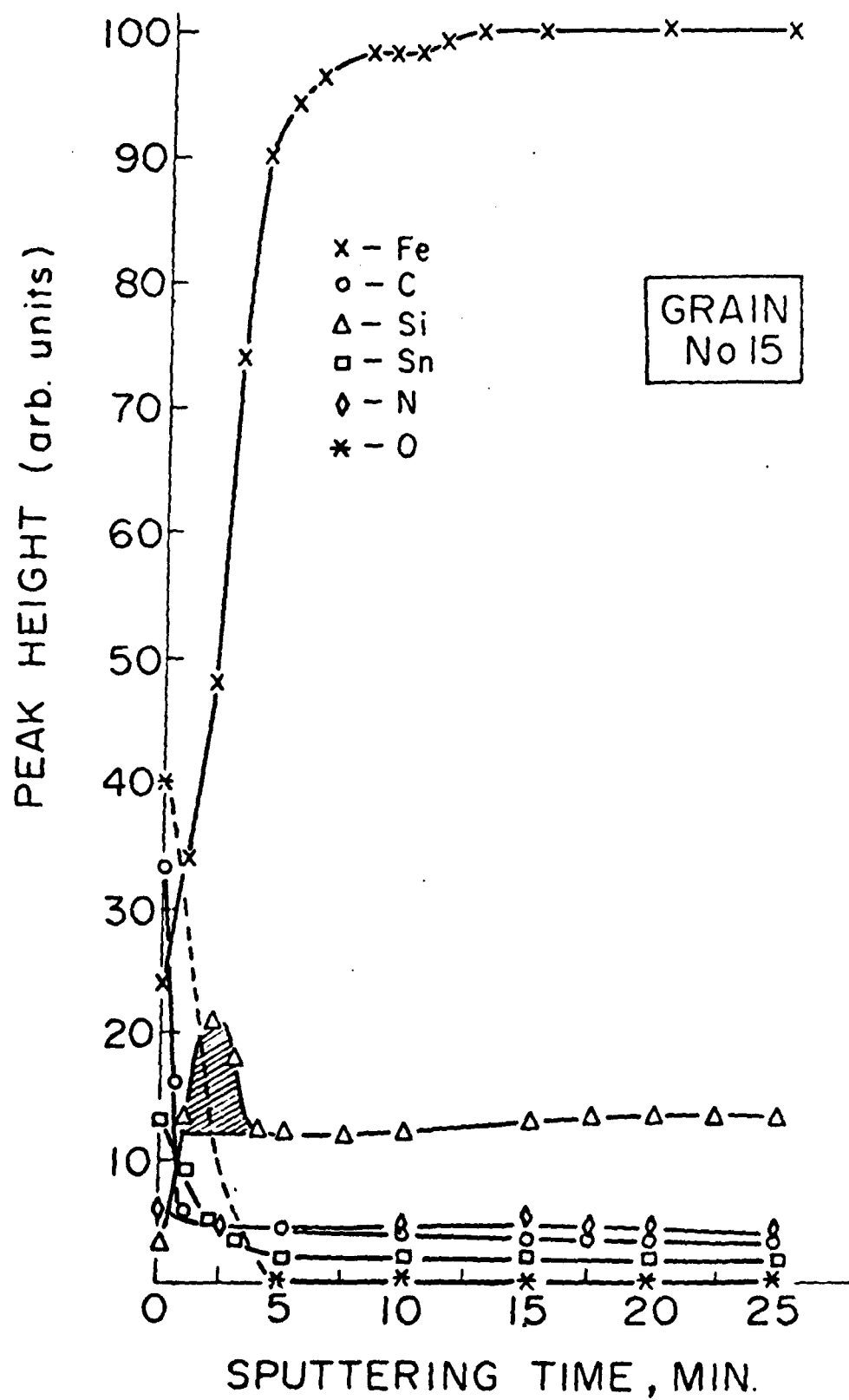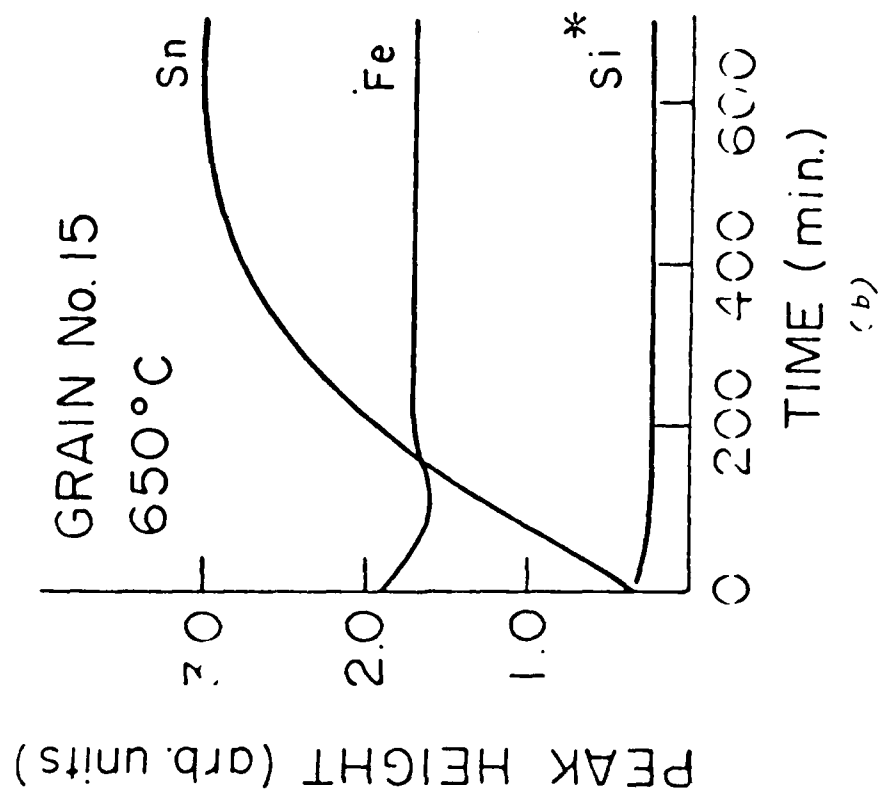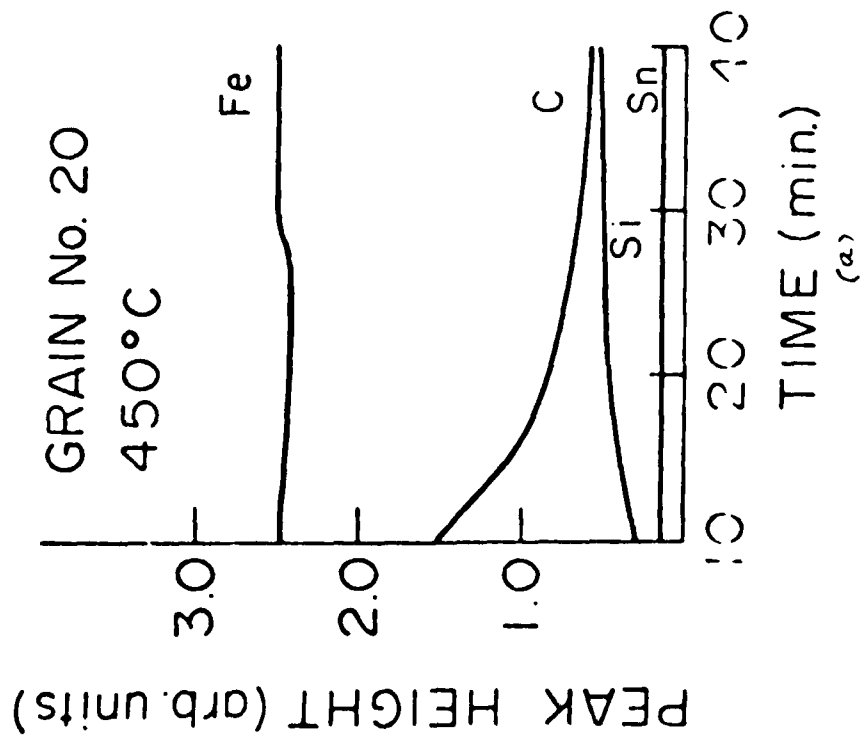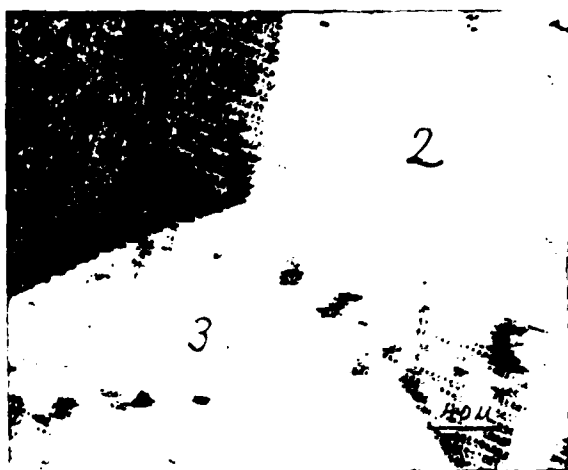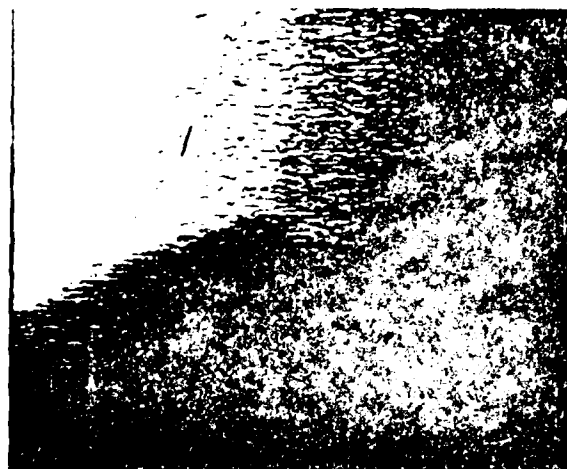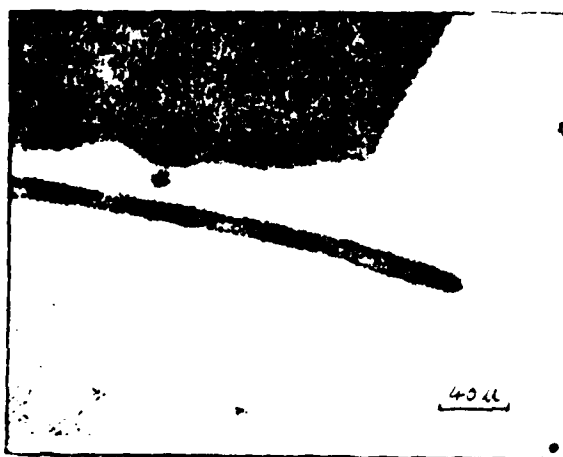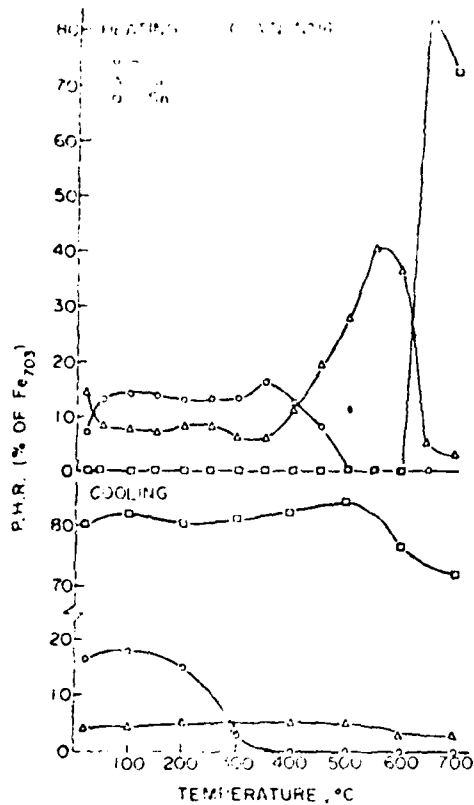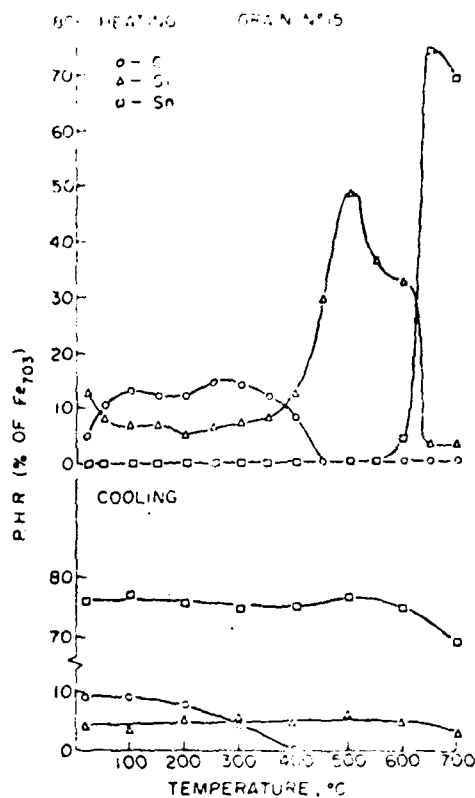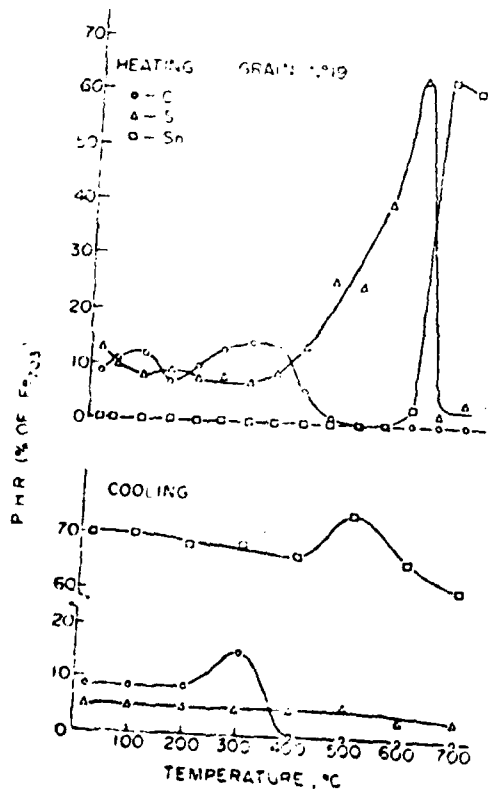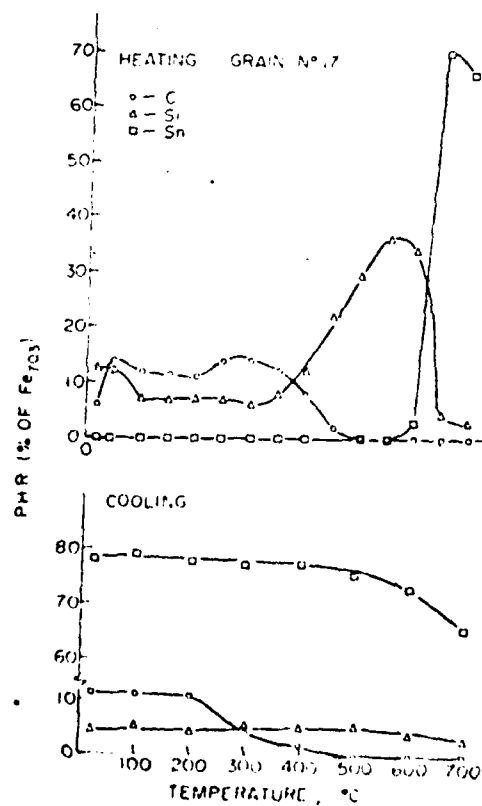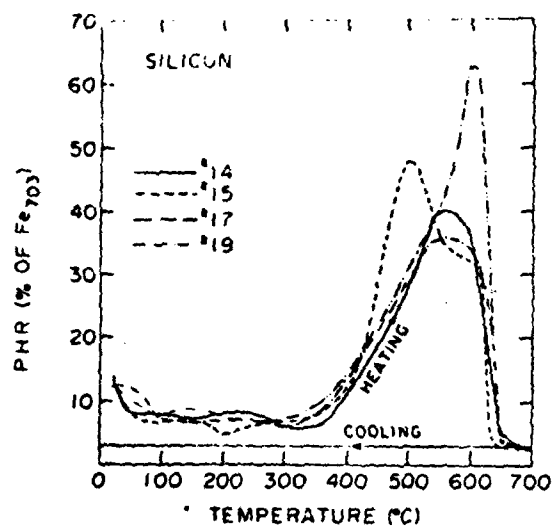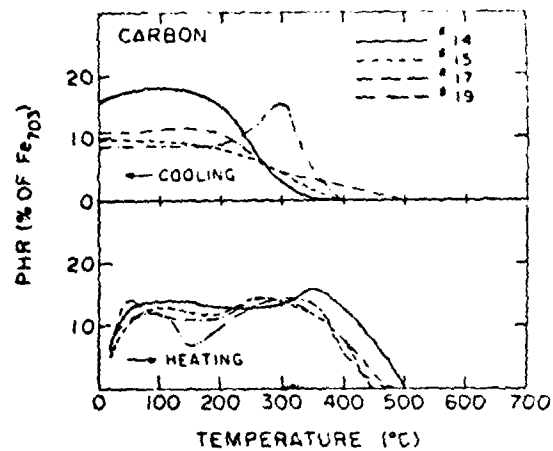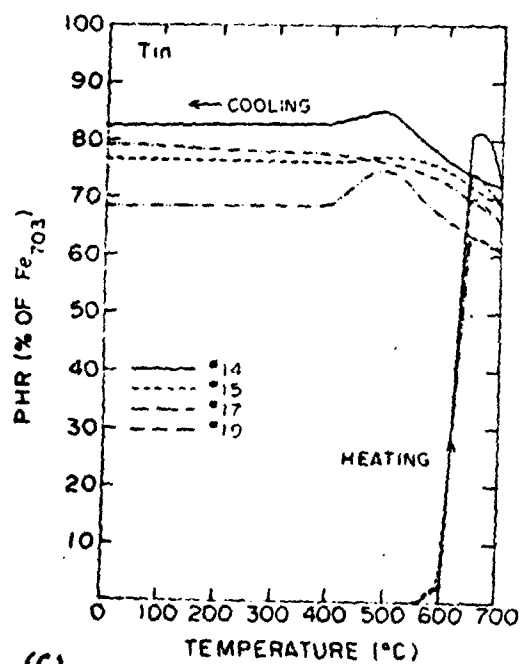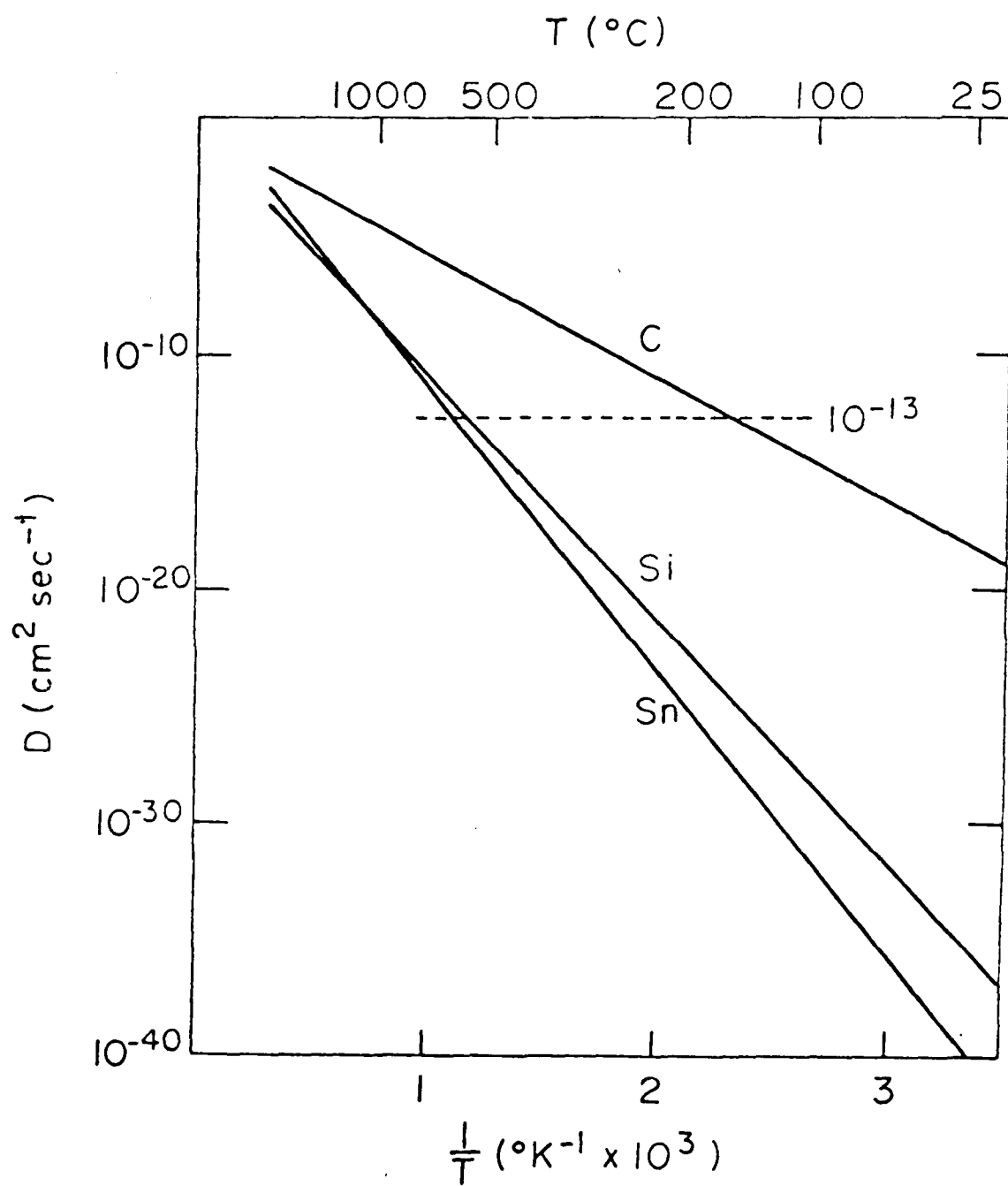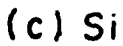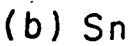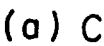
Fig 11

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